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AN EXPERIMENTAL STUDY OF LiH STOICHIOMETRY AT ELEVATED TEMPERATURES AND PRESSURES

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June 25, 1975

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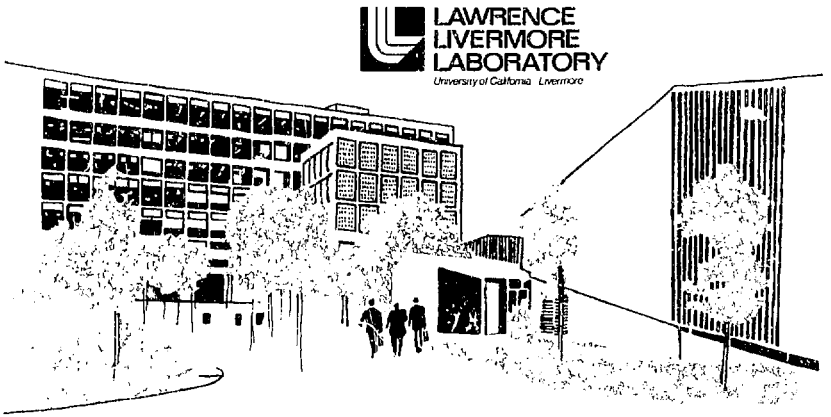

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Abstract

We have investigated the stoichiometry of LiH in the temperature interval 500 - 900 K at hydrogen pressures between 2.5 and 6.0 GPa. The results and interpretation of these experimental data are complicated by the presence of ubiquitous intermetallic compounds from encapsulating materials, which are formed at pressures below 4.0 GPa. The most definitive results of the investigation were produced in an assembly that consisted of a Ag-Pd inner capsule and tantalum outer capsule at a pressure of 5.0 GPa and 733 K. This run produced no change in LiH stoichiometry, nor any change in the NaCl-type crystal structure. As a result of our investigation, we conclude that up to a pressure of 6.0 GPa and a temperature of 803 K no quenchable LiH_n with $n > 1$ can be produced.

Introduction

Under suitable conditions elemental lithium reacts with hydrogen to form stoichiometric LiH. We have conducted a reconnaissance study to determine if LiH reacts further with hydrogen to form a quenchable nonstoichiometric LiH_n, where $n > 1$. We have treated the ordinary hydride with hydrogen at pressures between 2.5 and 6.0 GPa in the temperature interval 500 - 900 K. In addition to these experiments we have investigated the effect of time on LiH stoichiometry under these conditions. This report contains the results of these experiments. All data are reported in SI units.

Experimental Procedures

All experiments below 4.0 GPa were performed in a piston-cylinder apparatus similar to that of Boyd and England[1]. The high pressure die-and-sample assembly have been previously described by Stephens[2] and Stephens et al.[3] Figure 1 is a schematic illustration of the die and internal capsule arrangement we employed in all our experiments. Temperature was measured using chromel-alumel thermocouples without pressure correction. Accuracy of all temperature readings is ± 20K. Pressures are accurate to ± 0.1 GPa.

The experiments conducted above 5.0 GPa were carried out in a 12.7-mm × 12.7-mm girdle anvil device previously described by Stromberg and Stephens[4,5]. In this apparatus, temperature was measured by

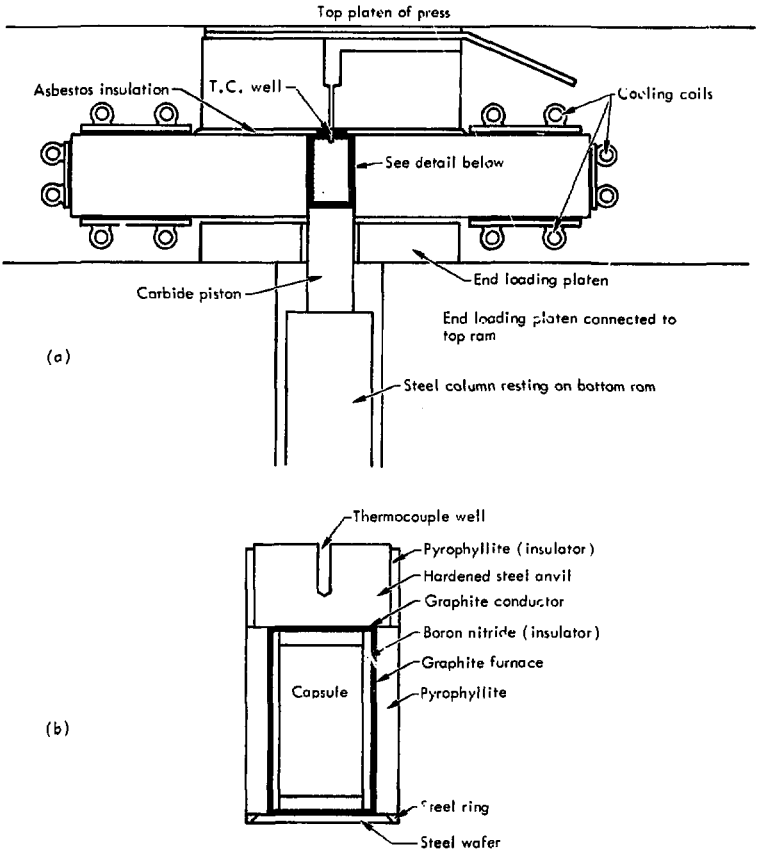

Fig. 1 High-pressure-die assembly in press, schematic. (a) Overall view, (b) Detail of capsule holder.

monitoring wattage input which previously had been calibrated by H. D. Stromberg[6] as a function of temperature using a $Mo-Mo_{50}$ Re thermocouple (see Fig. 2). Accuracy of all readings is ± 15 K.

Run products were analysed by x-ray powder diffraction techniques. The sample capsules were sawed open in an argon-atmosphere glove box. The material was then pulverised and the samples sealed in thin-walled glass capillaries for use in Debye-Scherrer cameras. LiH gives a simple diffraction pattern of the fcc NaCl type so that diffraction lines due to other materials can be easily recognised. Because of faulty seals LiOH impurities were observed on rare occasions in some diffraction patterns. These patterns were excluded from further consideration.

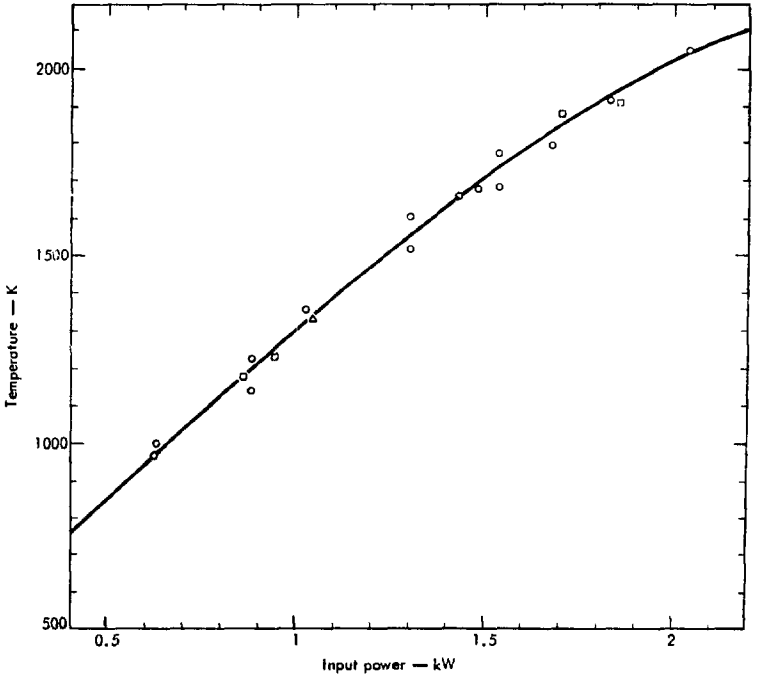

Fig. 2 Girdle temperature calibration using $Mo-Mo_{50}Re$ thermocouple. See Ref. 6.

X-ray diffraction analyses were carried out by manual or computer searches of the Joint Committee for Powder Diffraction Standards inorganic file consisting of approximately 15,000 standard patterns. Some of the run products were analysed for metal impurities either by emission spectroscopy or x-ray fluorescence techniques.

Sample Preparation and Containment

One of the most vexing and complex aspects of the high pressure investigation was the fabrication of suitable capsule arrangements and formulation of experimental procedures to achieve successful runs. Because of the reactive nature of the materials employed, as well as the multiplicity of problems encountered, we shall discuss our efforts in this area in detail.

The early experiments were performed utilizing an internal gold capsule whose geometry is schematically illustrated in Fig. 3. Powdered LiH was contained within an Armco iron inner capsule. This was surrounded by powdered BeH_2, and both components were contained in a sealed gold capsule. This arrangement will be called Design 1. This, as well as successive capsule designs, occupies the "capsule" cavity illustrated in Fig. 1b.

The thesis underlying these early experiments was that, at sufficiently high temperatures, the $BeH_2 \rightarrow Be + H_2$ reaction would occur in the outer capsule[7]. The hydrogen would then permeate through the steel liner and react with the LiH. This experimental arrangement was only partially successful. Hydrogen gas was indeed liberated at elevated temperatures; however, the thin gold outer capsule was too weak to contain the extreme internal pressures.

Design 2, an attempt to remedy this situation, is schematically illustrated in Fig. 4. The big change is the nature of the outer gold capsule. In Design 2, it is a solid capsule 15.9 mm wide with a 3.18-mm wall thickness, whereas in Design 1 wall thickness was only 0.76 mm. In

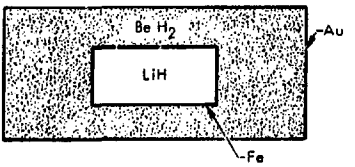

Fig. 3 Capsule design 1.

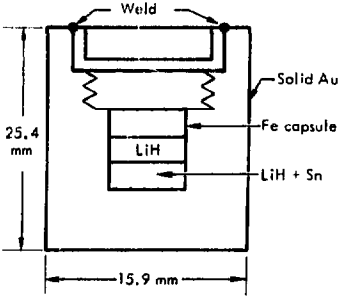

Fig. 4 Capsule design 2.

addition, Design 2 was different in that it generated hydrogen by reaction of a mixture of metallic tin and LiH loaded in the outer capsule.

Design 2 was structurally sound and was used in several runs. Contamination of the products by lithium-gold intermetallic compounds was a serious drawback, however.

The appearance of this contaminant phase prompted further modifications, with austenitic stainless steel, Armco 21-6-9 (21Cr-6Ni-9Mn), replacing the solid gold outer capsule. This steel is much stronger than gold and recent tests reveal extreme resistance to hydrogen embrittlement[6-10]. Chemical analysis of the material tested by Frick et al.[8] is provided in Table 1. Design 3 is given in Fig. 5. Design 3 was successfully employed in several experiments; it deterred gold-lithium intermetallic compound formation and provided high strength to prevent capsule rupture.

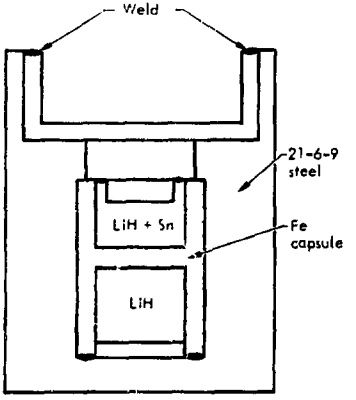

Fig. 5 Capsule design 3.

Table 1. Composition of Armco 21-6-9[a] (in element wt %).

	Bar	Plate
C	0.033	0.03
Si	0.11	0.37
Mn	8.86	8.88
Ni	6.66	6.62
Cr	19.7	20.02
Mo	----	----
P	0.022	0.020
S	0.011	0.013
Cu	0.19	0.23
N	0.29	0.33
Fe	Balance	Balance

[a]Data from Frick et al.[8]

Experimental Results

Table 2 lists results of all experiments that, in our opinion, produced hydrogen under conditions of the run. X-ray diffraction results appear in Table 3.

Runs 4 and 5 lasted for only a matter of minutes and were aborted because of electrical shorts in the high pressure system. This problem was overcome in Run 6 by using mica and asbestos paper between the die and back-up block and by placing cooling coils around the die assembly (see Fig. 1). Typical die temperatures encountered in longer runs using the cooling coils are portrayed in Fig. 6, which plots die temperature as a function of time for Run 6.

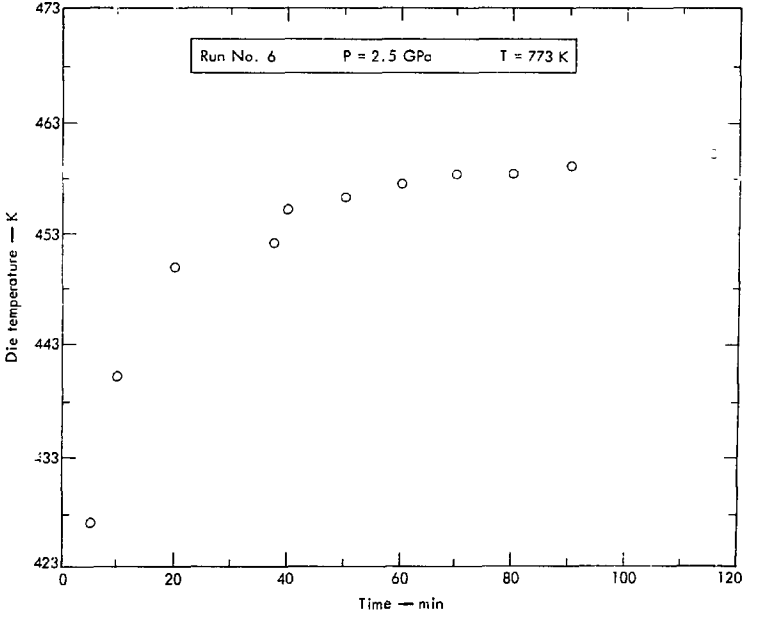

Fig. 6 Die temperature as a function of run duration for experiment No. 6.

Table 2. Experimental Runs on Lin.

Run no.	Press. GPa	T K	Time hr	Starting material	Outer capsule	Inner capsule	Inner capsule "mix"	Sample desired	X-ray diffraction analysis	Comments
4	2.5	575	0.16	Powdered LiH	Au capsule wall thickness 0.76 mm	Armco iron wall thickness 0.76 mm	LiH+Sn	1		Aborted due to electrical short in system. Rate of sample temperature increase too great, i.e., sample temperature reached 300°C in 0.01 hr - short circuit in system at initial application of pressure to assembly.
5	2.5	773	0.067	Powdered LiH	Solid Au with wall thickness of 0.15 mm	Armco iron with 1.73 mm wall thickness	LiH+Sn	1	X	Aborted due to electrical short in system.
6	2.5	773	1.0	Powdered LiH	Solid Au	Armco iron	LiH+Sn	2		Successful. Teflon insulator was employed on top of upper die and cooling coils were employed around entire die assembly to prevent overheating and possible electrical shorts.
7	2.5	893	0.33	Powdered LiH	Solid Au	Iron	LiH+Sn	2	X	Successful.
8	2.5	773	0.1	Powdered LiH	Solid Au	Iron capsule welded at both ends	LiH+Sn	2	X	Successful.
9	2.5	773	0.16	Powdered LiH	Solid steel alloy 21-6-9	Iron capsule welded at both ends	LiH+Sn	3	X	Successful.
10	2.5	773	2.0	Pressed pellet of LiH	Steel alloy 21-6-9	Iron capsule welded at both ends	Pressed pellet of LiH+Sn	3	X	Successful.
11	2.5	573	.10	Pressed pellet of LiH	Steel alloy 21-6-9	Iron capsule welded at both ends	Pressed pelle of LiH+Sn	3		Aborted due to collapse and shattering of back-up Block on die assembly.
12	2.5	773	7.83	Pressed pellet of LiH	Steel alloy 21-6-9	Iron capsule welded at both ends	Pressed pellet of LiH+Sn	3	X	Successful.

Table 2. (cont'd)

Run no.	Press. GPa	T K	Time hr	Starting material	Outer capsule	Inner capsule	Inner capsule mix[a]	Sample design	X-ray diffraction analysis	Comments
13	2.6	773	2.0	Pressed pellet of LiH	Steel alloy 21-6-9	Nickel capsule	Pressed pellet of LiH+Sn	3	X	Successful.
14	2.4	773	0.25	Pressed pellet of LiH	Steel alloy 21-6-9	Ag-Pd	Pressed pellet of LiH+Sn	3	X	Successful, but 21-6-9 extremely embrittled, Ag-Pd changed color to bronze.
15	5.0	773	0.50	Pellet of LiH	Tantalum	Platinum inner capsule unwelded	LiH+Sn	4	X	Successful.
16	6.0	803	0.16	Pellet of LiH	Tantalum	Platinum inner capsule unwelded	LiH+Sn	4	X	Successful.
17	5.0	773	0.50	Pellet of LiH	Tantalum	Ag-Pd inner capsule	LiH+Sn	4	X	Successful.

[a] In the case of girdle-anvil runs 15, 16, and 17, LiH + Sn is the outer capsule mix. There was no inner mix used in sample design 4.

Runs 6, 7, and 8 were completed successfully using Design 2. Run products for these experiments, which were performed at 2.5 and 3.5 GPa, were complicated by the presence of large quantities of gold-lithium intermetallic compounds (see Fig. 3). In particular, the Au_3Li is of the Cu_3Au structure type[11] with a = 396.8 pm. The strong contaminant lines overshadowed several weak diffraction lines which we could not identify. Table 3 lists the unknown present in Runs 6, 7, and 8 as phase X.

Run 9 was undertaken to test the feasibility of using Armco 21-6-9 as capsule material at elevated temperatures and pressures in an attempt to suppress the formation of gold-lithium intermetallic compounds. The components of the experiment consisted of a

- small inner mild-steel capsule welded at both ends to provide a closed system,
- a large mass of LiH + Sn surrounding the mild steel capsule, and
- a large outer capsule composed of the 21-6-9 alloy.

Table 3. Debye - Scherrer x-ray powder diffraction results of experimental runs on LiH.[a]

Run No.	State of LiH	Other phases present	Comments
5	Normal, stoichiometric LiH	Strong amounts of probably Au_3Li in addition to small quantities of a gold-rich gold-lithium solution. Weak diffraction lines of unknown phase X.	The stoichiometric LiH is present in small amounts. The Au_3Li is of the Cu_3Au structure type with a = 397.1 pm; the terminal Au-Li solid solution has a = 396.8 pm. See Ref. 11.
7		Essentially identical to Run 5	
8		Essentially identical to Run 5	
9	Normal, stoichiometric LiH	Stainless steel and SiC. Au-Li intermetallic compounds are absent.	New steel and carbide impurities probably introduced when capsule was mechanically opened.
10	Normal, stoichiometric LiH	Stainless steel and SiC. Au-Li compounds are absent. Diffraction lines of new phase Y. Emission spectroscopy shows there heavy metal impurities; Sn>3 wt.% Fe 0.3 wt.%; Ni 0.3 wt.%.	Phase Y diffraction lines are not found in a reference library containing approximately 15,000 patterns. Approximately 50% of unknown lines are accounted for in a rough manner by $Li_3Na_3Co_2F_{12}$. Phase Y could possibly contain some $Li_3Fe_2(LiH_4)_3$ or $Li_3Sn_2(LiH_4)_3$.
12	Normal, stoichiometric LiH	New set of weak diffraction lines, phase Z, distinct from fcc LiH and from phase Y lines. Emission spectroscopy shows: Sn $\geq$ 2 wt.%, Fe $\geq$ 0.4 wt.%.	New phase Z lines correspond to no presently known structure.
13	Normal, stoichiometric LiH	Austenite or Ni_xC, x > 4 and strong amounts of unknown phase. Fluorescence analysis shows: Ni strong; Ca, Fe, As, Zr trace.	Strong amounts of new unknown phase or phases; product is dark gray.
14	Doubtful normal LiH	Lines of unknown phase. Fluorescence analysis shows: Major; Pd, Ag less strong, Minor; Pt, Ni, Zr, Mo.	Very complex diffraction pattern. Product is dark in color.

Table 3. (cont'd)

Run No.	State of LiH	Other phases present	Comments
15	Normal, stoichiometric LiH	Other unknown phase; Fluorescence analysis shows: Major; Pt, Zn, Minor; Sr, Zr, Fe.	Very complex diffraction pattern. Strong amount of normal LiH. Product is light.
16	Normal, stoichiometric LiH	Lines due to Pt and Ta.	Relatively simple and "clean" pattern; all diffraction lines accounted. Strong LiH present.
17	Normal, stoichiometric LiH	Primitive cubic phase almost certainly $AgPd_3$. Fluorescence analysis shows: Ag, Pd strong; Zn less strong.	Relatively simple and "clean" pattern. Strong amounts of normal LiH and weak amounts of primitive cubic phase with lattice constant = 393 pm. Product is light in color.

[a]Fluorescence analysis provided by R. Ryon.

Data reported in Table 2 indicate that the capsule survived 10 min at 2.5 GPa and 773 K. X-ray Diffraction analysis (see Table 3) detected no gold-lithium intermetallic compounds.

Encouraged by the performance of the 21-6-9 alloy, we made runs 10 and 12 for 2 and 7.83 hours, respectively, using Design 3 in order to assess the effect of time at elevated temperature and pressure on the stoichiometry of LiH. Both runs produced extremely complicated results (see Table 3). Run 10 contained a new set of diffraction lines, which we are presently terming phase Y. Running a computer search utilizing a reference library containing approximately 15,000 known patterns resulted in no unequivocal identification of Phase Y. Approximately half of the unknown lines are accounted for in a general way by $Li_3 Na_3 Co_2 F_{12}$, a flouride garnet. Run 12 (see Table 3) produced another new set of diffraction lines. This set, much weaker in intensity than those characteristic of Phase Y, are being called Phase Z. We are currently unable to account for the Phase Z lines in terms of any known structure. A spectrochemical analysis of runs 10 and 12 appears in Table 4.

Because of the unknown phases present in runs 10 and 12, we decided to modify the inner capsule material and assess the utility of nickel and Ag-Pd. Runs 13 and 14 were performed at the 773 K isotherm and 2.6 and 2.4 GPa, respectively, using nickel and Ag-Pd. Data presented in Table 3 reveal that both experiments produced very complicated x-ray diffraction patterns, in addition to normal LiH. Apparently, substitution of nickel and Ag-Pd for the 21-6-9 alloy did not supress the formation of contaminant phases.

In view of the failure to produce uncontaminated run products at pressures between 2.4 and 3.5 GPa, we decided to

Table 4. Spectrochemical analyses of LiH runs no. 10 and 12.[a]

Analysis:	10	12
Sn	>30,000	≥20,000
Fe	3,000	4,000
Ni	3,000	100
Mn	900	200
Cr	150	200
Si	200	150
B	150	100
Cu	150	70
Ca	30	40
Al	30	20
Bi	15	nd<10[b]
Ag	< 3	10
Be	≤ 9	nd< 4
Mg	6	7
Sr	3	< 4

The following elements were not detected in either sample:

<4000	K
<400	As, Hg
<100	Cd, Ce, Na, P, Sb, Th, Zn
<40	Nb
<10	Ba, Ge, Mo, Pb, Ti
<4	Co, In, V, Zr

[a]Values are approximate ppm by weight for the impurity elements listed.

[b]nd - not detected.

Analyst: E. Peck

perform a series of runs at pressures between 5.0 and 6.0 GPa. Runs 15, 16, and 17 were carried out in a girdle anvil device using capsule design 4 (see Fig. 7). Tantalum served as the outer capsule material; platinum and Ag-Pd were the inner capsule components. Results of these experiments are listed in Tables 2 and 3. Run 15 (5.0 GPa/773 K) produced a variety of unknown phases with complicated x-ray diffraction patterns. Runs 16 and 17 were successful; they produced materials that yielded simple and "clean" patterns. Run 16 (6.0 GPa/803 K) product gave a strong normal LiH pattern with small amounts of Pt and Ta as contaminants. Run 17 (5.0 GPa/773 K) product also gave strong indication of normal LiH. However, it contained traces of what seems to be a primitive cubic phase, almost certainly $AgPd_3$, possessing a lattice constant of 393 pm. X-ray fluorescence analysis indicated that Run 17 contained small amounts of zinc.

Thus, we see that of all the experiments performed, the least contaminated was Run 17. Table 3 shows that it contained no other form of LiH than the normal.

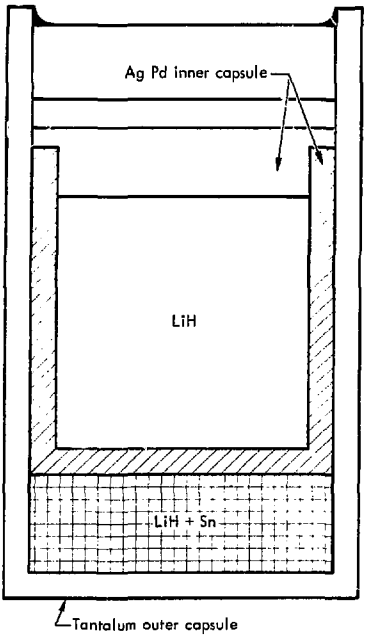

Fig. 7 Capsule design 4.

Discussion

We have investigated the stoichiometry of LiH in the temperature interval 500 - 900 K between 2.5 and 6.0 GPa. The results and interpretation of these experimental data are complicated by the nature and multiplicity of contaminating intermetallic compounds formed at pressures lower than 4.0 GPa.

The most definitive results of the investigation were produced in an assembly that consisted of a Ag-Pd inner capsule and tantalum outer capsule at a pressure of 5.0 GPa and 773 K. This run produced no change in LiH stoichiometry, nor any change in the NaCl-type crystal structure. As a result of our investigation, we conclude that up to a pressure of 6.0 GPa and a temperature of 803 K no quenchable LiH_n with $n > 1$ occurs.

It is well known that many compounds possessing the rock salt structure transform into the CsCl structure at elevated pressures. Employing two diverse potential functions, Schumacher[12] calculated that LiH would undergo a phase transition between 0.305 and 0.380 GPa. His calculation is predicated on the fact that LiH is an ionic solid. Our results do not verify Schumacher's theoretical predictions; at least such a phase cannot be retained at ambient temperatures and pressures. Olinger and Halleck[13] recently found that LiH "retains the low pressure NaCl structure to 12 GPa." However, Johnson[14] mentioned that indirect evidence from shock wave experiments suggested the possibility of a transformation at pressures greater than 12 GPa. If this transition is confirmed, it still remains to be determined whether LiH possessing the CsCl structure could exhibit nonstoichiometry.

Acknowledgements

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References

1. F. Boyd and J. England, "Development of High-Pressure Apparatus," in Annual Report of Director of Geophysical Laboratory, Yearbook 57 (1958) pp. 170-173.
2. D. Stephens, J. Geophys. Res. 69 (14), 2967 (1964).
3. D. Stephens, E. Lilley, and H. Louis, Intern. J. Rock Mech. Min. Sci. 7, 257 (1970).
4. H. D. Stromberg and D. Stephens, Bull. Am. Ceram. Soc. 49 (12), 1030 (1970).
5. H. D. Stromberg and D. Stephens, Process for Producing Sintered Diamond Compact and Products, U.S. Patent 3,574,580 (1971).
6. H. D. Stromberg, Lawrence Livermore Laboratory, unpublished results (1966).
7. W. Mueller, J. Blackledge, and G. Libowitz, Metal Hydrides (Academic Press, New York, 1968) pp. 235 and 554.
8. V. Frick, G. Janser, and J. Brown, "Enhanced Flawgrowth in SSE Main Engine Alloys in High Pressure Gaseous Hydrogen," in Space Shuttle Materials, vol. 3 (Society of Aerospace Materials and Process Engineers, 1971) pp. 567-604.
9. H. Gray, Hydrogen Environment Embrittlement, NASA Technology Memorandum TMX-68088 (1972).
10. R. Vandervoort, Metals Eng. Quart. 2, 10 (1972).
11. W. Pearson, A Handbook of Lattice Spacing and Structures of Metals and Alloys, vol. 2 (Pergamon Press, 1967).
12. D. Schumacher, Phys. Rev. 126 (5), 1679 (1962).
13. B. Olinger and P. Halleck, App. Phys. Lett. 24, 536 (1974).
14. Q. C. Johnson, Lawrence Livermore Laboratory, private communication (1974).

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